

# **Study of Acidic Organic Salts in Catalysis and Nanomaterial Synthesis**

A thesis submitted in partial fulfilment of the requirements  
for the award of the degree of

**Doctor of Philosophy**

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## Chapter 6

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### *Conclusion & Future Scopes*

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## 6.1. Summary of the present work

This thesis tried to offer substantial study about development of ionic liquid-based materials of the cyclic/acyclic ammonium and imidazolium-cations with incorporation of special ‘task-specific’ properties like Brønsted-Lewis acidic nature, redox behaviour *via* tethering or incorporation of acidic functionalities like direct N-SO<sub>3</sub>H groups or complex metal halide anions to the constituent ions of organic salts. These structural changes in the synthesized cyclic/acyclic ammonium and imidazolium-based organic salts modified the inter/intra-molecular interactions, providing them with extensive thermal and chemical stabilities as well as the required task-specific properties of added functional groups. The replacement of halide anions of sulfonic acid functionalized piperazinium salt with complex transition metal chloride anions provided Brønsted-Lewis acidic character to the organic-inorganic halometallates for catalytic study of multicomponent synthesis of nitrogen heterocycles. Likewise, the combinations of sulfonic acid functionalized ammonium/imidazolium cations with the permanganate anion developed moisture-stable and thermally stable solid acidic organic-inorganic hybrid permanganate based redox catalysts for oxidation of alcohols and organic sulfides under environmentally benign methods. Additionally, the task-specific properties of sulfonic acid functionalized organic salts used for fabrication of narrow bandgap displaying heterostructured nanocomposites of ZnO with Ag/Ag<sub>2</sub>O to get improved photocatalytic efficiencies in the region of visible light to degrade organic pollutants such as dyes.

The major findings of this thesis are highlighted chapter wise as given below:

### Chapter 1A

- It provided a relevant overview of ionic liquids, and their unique properties based on the constituent ions with a general introduction of their various classes.
- One unit discussed the designing of functionalized ionic liquids/organic salts and their significance as functional materials for special applications in catalysis, electrochemistry, separation techniques, organic and/or inorganic synthesis, analytical techniques, industrial purpose etc.
- As a functional material, the synthesis of metal containing ionic liquids was discussed briefly with significant applications such as Lewis acid catalysts, Brønsted-Lewis acidic materials, oxidizing agents, photocatalysts etc.

- It also included the stabilizing effects of ionic liquids for fabrication of metal nanoparticles with variation of the structural compositions of organic salts as reaction medium or template.
- Furthermore, it gave descriptive literature review on the synthesis of permanganate based organic-inorganic hybrids, synthesis of heterostructured metal nanomaterials in ionic liquids, synthesis of quinazoline derivatives, oxidation of alcohols and organic sulfides by permanganate-based hybrids and organic pollutant degradation by Ag based ZnO nanocomposites.

## Chapter 1B

- **Chapter 1B** gave an overview of the materials and methods used while carrying out the works related to this thesis.

## Chapter 2

- Three organic salts of N,N'-disulfopiperazinium cation with complex metal chloride anions of Fe(III), Ni(II) and Co(II) were developed as Brønsted-Lewis acidic hybrid solid materials.
- Their structural compositions were established by FT-IR, UV-Visible DRS, SEM, EDX, Powder-XRD and Raman techniques. Thermogravimetric analyses showed removal of physisorbed water around 100 °C for Fe(III) salt in contrast to 150-170 °C for Ni(II) & Co(II) organic salts for strongly bound water molecules in a highly crystalline state.
- Their relative Brønsted acidities were determined from UV-visible Hammett plots while Lewis acidity strength was observed via FT-IR spectra of these salts in presence of pyridine as probe molecule.
- The catalytic activities of these acidic organic salts were investigated for a one-pot three-component synthesis of 1,2-dihydroquinazolines as recyclable heterogeneous catalysts.
- The plausible mechanism showed synergistic effects of both Brønsted and Lewis acidic sites in the halometallate catalysts for the enhanced acidity to carry out the reaction.

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**Chapter 3**

- In this chapter, an organic-inorganic permanganate hybrid [MDSIM][MnO<sub>4</sub>] of 2-methyl-1,3-disulfoimidazolium [MDSIM]<sup>+</sup> cation was prepared as solid material *via* ion exchange reaction of 2-methyl-1,3-disulfoimidazolium chloride ([MDSIM]Cl) ionic liquid with KMnO<sub>4</sub> at room temperature.
- Structural composition of the hybrid was established by FT-IR, UV-Vis DRS, PXRD, Raman studies and SEM, EDX, elemental mapping images.
- Thermo-gravimetric analysis pointed out the extensive thermal stability of the hybrid, whereas SEM images showed heterogeneous morphology of various sized crystalline granules.
- The material was investigated as recyclable homogeneous oxidative catalyst for controlled oxidation of primary/secondary benzyl alcohols to carbonyl compounds in 10% aqueous H<sub>2</sub>SO<sub>4</sub> and acetonitrile solution at 80 °C temperature and in solvent-drop grinding method at room temperature. The role of acid was identified as co-catalyst in oxidation reactions.
- Computational studies using density functional theory (DFT), regarding the optimized structure of the hybrid and proposed mechanism of oxidation reaction, also supported towards the efficacy of this recyclable material as catalyst as well as oxidant.

**Chapter 4**

- In this chapter, two organic-inorganic hybrids of permanganate anions namely N, N'-diethyldisulfoammonium permanganate [DEDSA][MnO<sub>4</sub>] and 1,4-disulfopiperazinium permanganate [DSPZ][MnO<sub>4</sub>]<sub>2</sub> were developed as thermally stable oxidants through ion exchange reactions of the respective organic chlorides with KMnO<sub>4</sub> salt at room temperature.
- Various spectroscopic and analytical techniques like FT-IR, PXRD, Raman, UV-Vis DRS, SEM and EDX were employed to confirm the structural compositions of both the hybrids.
- Comparative thermogravimetric analyses with reference to the parent organic chloride salts expressed substantial changes in their thermal stabilities as well as hydrophilic/hydrophobic properties.

- The oxidative efficiencies of the hybrids were investigated as recyclable homogeneous catalysts for selective formation of sulfoxides from organic sulfides in 10% aqueous sulfuric solution at 80 °C with decent to excellent yields.

## Chapter 5

- Fabrication of two heterostructured Ag/Ag<sub>2</sub>O integrated ZnO nanocomposites (**2a** & **2b**) were done in aqueous solution of sulfonic acid functionalized organic salts i.e. 1,4-disulfopiperazine-1,4-dium chloride ([DSPZ].2Cl) and 1,3-disulfoimidazolium chloride ([MDSIM]Cl).
- The analytical data of PXRD, SEM, EDX, Raman, UV-Vis DRS, TEM, XPS, BET etc. identified their structures as Ag/Ag<sub>2</sub>O/ZnO nanocomposites with different sized nanoparticles.
- Both the nanocomposites degraded the model dye methylene blue (MB) completely under the optimized dose of catalysts in basic medium (pH=10), whereas the degradation was less in acidic solution.
- In the mixture of MO+MB dye solution, methyl orange (MO) dye exhibited better photodegradation activity at all the studied pH than those by the MB dye, while in the mixture of MO+CV, both the dyes followed similar degradation patterns.
- The recovered photocatalyst was recycled for four consecutive runs with slight reduction of photocatalytic efficiencies for degradation of the model dye.

## 6.2. Future scopes of the present work

- Study of the catalytic activity of synthesized halometallates for one pot multicomponent synthesis of N, S and O heterocycles including oxazines, thiazine, triazine etc.
- More structural variations in designing of permanganate based organic-inorganic hybrid oxidants using variation of the organic cations such as pyrrolidinium, piperidinium, phosphonium etc.
- Investigation of oxidative behaviour of the hybrids towards oxidation of other functional groups such as olefins and carbonyl compounds.
- Fabrication of mono/bi-metallic nanocomposites in ionic liquids/organic salts to use them in various catalytic reactions.

- Investigating the mechanistic study for degradation of pesticides and antibiotics using fabricated Ag/Ag<sub>2</sub>O/ZnO nanocomposites.